High Temperature GPC of Polypropylene

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Synopsis

The highest temperature at which molecular weight distributions can be characterized by current techniques is 145°C. Supermolecular aggregates may exist at this temperature in polypropylene solutions in trichlorobenzene and other solvents. Dissolution procedures at higher temperatures are ineffective in this case because of the limited thermal stability of polypropylene. Aggregate-free solutions can be prepared, however, by controlling storage times at 145°C in mixtures with added stabilizers. Low angle laser light scattering measurements can be used to determine when true solutions have been produced. This occurs when measured second virial coefficients agree with values predicted for the $\overline{M}_w$ measured in the light scattering experiment. GPC–LALLS measurements of $\overline{M}_w$ and $\overline{M}_z$ provide similar information about the effects of storage time on dissolution of aggregates and polymer degradation.

INTRODUCTION

Molecular weight analyses require the polymer molecules to be in true solution, i.e., dispersed on a molecular level. This condition is not realized in some cases where stable intermolecular aggregates may persist in mixtures of macromolecules and solvents. In such instances a dynamic equilibrium is not achieved between aggregated and isolated polymer molecules and the concentration and size of aggregates is not appreciably affected by solution concentration.

Stable aggregates have been shown to present a problem in the molecular weight characterization of poly(vinyl chloride)[1,2] and polyethylene.[3]

A simple and reliable procedure for the preparation of aggregate free solutions of polyethylene has been reported from our laboratory.[4] Development of a similar procedure for polypropylene presents particular problems because polypropylene has a higher crystal melting range and poorer thermal stability than polyethylene. The work summarized in this article was undertaken to find appropriate conditions for the preparation of aggregate-free solutions of polypropylene. The thermal stability of this polymer was also monitored in order to ensure that the experimental procedures did not cause degradation of the polypropylene.

The method reported here is a convenient and necessary step in the molecular weight analyses of polypropylene.

EXPERIMENTAL

A Chromatix KMX-16 laser differential refractometer and a KMX-6 LALLS (low angle laser light scattering) photometer attached to a Waters

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150C high temperature gel permeation chromatograph were used in this work. The LALLS unit was employed with an angle of 6–7° and a 0.15 mm field stop to minimize background. In experiments that were intended only to establish solution quality no columns were used in the gel permeation chromatograph. Only the pump and automatic injector of that unit were used. Samples of polypropylene solutions, prepared as described below, were injected into the LALLS unit at 145°C, and their light scattering properties were measured as they flowed through the KMX-6.

Experiments with the LALLS unit alone were used to determine the proper dissolution time for the preparation of aggregate-free solutions. Experiments with the GPC columns included were intended to establish the exposure limits to heat beyond which degradation of the polymer occurred.

Sample solutions for injection were stabilized with 0.1% (w/v) Irgafos D13-168 (2,4-di-*tert*-butylphenylphosphite) and 0.1% (w/v) Ionol (butylated hydroxytoluene). Antioxidants were not added to the eluant.

All solutions were made up in trichlorobenzene (TCB). Concentrations were 0.8–2.0 g/L in the off-line (no GPC columns involved) experiments and 1.5–3.5 g/L in the on-line experiments.

With polyethylene,[4] the absence of aggregates was established by the appearance of clean traces in off-line LALLS measurements and by the agreement of light scattering second virial coefficients with those predicted by the Kok–Rudin model.[5] Good solutions were obtained by heating polyethylene samples in trichlorobenzene for various periods at 165°C before making molecular weight measurements at 145°C.[4,6,7] Direct translation of this method to polypropylene proved to be impossible. Polypropylene solutions in TCB heated at 170°C for less than about 3 h plugged the pumping system when attempts were made to analyze them at 145°C. Solutions that were heated for longer periods discolored and were not analyzed because of this evidence of degradation.

Two commercial polypropylene homopolymers were used in this study. Their melt flow indices were 3 and 12, respectively. Mark–Houwink coefficients are required in the prediction of second virial coefficients.[5] For polypropylene in TCB, the preexponential constant was taken to be 1.52×10^{-2} dL/g with an exponent $= 0.76$.[8] Experimental values of the second virial coefficient, A_2, were obtained in off-line experiments according to the equation:

$$\frac{K_c}{R_\theta} = \frac{1}{\overline{M}_w} + 2A_2C \qquad (1)$$

where K, an optical constant, is a function of the specific refractive index increment of the solution, R_θ is the excess Rayleigh scattering of the solution over the solvent, c is the polymer concentration, and $\overline{M}_w$ is the weight average molecular weight of the polymer.

The specific refractive index increment for this solution was measured as -0.092 mL/g and -0.094 mL/g for the 3 melt index and 12 melt index polymers, respectively.

On-line experiments were performed with silanized porous silica columns and an eluant flow rate of 1.0 mL/min.

RESULTS AND DISCUSSION

In order to produce aggregate-free solutions without degradation of the polypropylene, a study was made of the relation between dissolution time in TCB at 145°C and light scattering second virial coefficients. These experiments, which were made by pumping polymer solutions through the LALLS unit without the use of GPC columns, were carried out every 2 h, starting with an initial dissolution time of 5 h.

Light scattering experiments with polyethylene mixtures[4,6] have shown that solutions containing aggregates produce low values of A_2 but that the measured $\overline{M}_w$ is little affected. Thus, the intercept of the right hand side of eq. (1) can be used to estimate $\overline{M}_w$ and this molecular weight average can be used with the Kok–Rudin theory[5] to calculate the corresponding second virial coefficient. The measured and predicted A_2 values agree well when the solution has been freed of aggregates.

The same criterion was used to assess polypropylene solutions. As can be seen from Figure 1, the experimental value of A_2 is lower than that predicted for the solutions made by dissolution for 25–30 h at 145°C. After about 30–33 h (longer for higher molecular weight polymers) the experimental A_2 coincides with that estimated from the measured $\overline{M}_w$ and the Mark–Houwink coefficients for polypropylene in TCB. It is interesting also that LALLS traces become free of "spikes" that have been attributed to agglomerates[4] after dissolution times slightly shorter than those that produce agreement of measured and theoretical A_2's.

The experimental second virial coefficients remain stable in these solutions for another 15–20 h (less for higher molecular weight polypropylenes). There follows a sharp increase in A_2 and a decrease in the measured $\overline{M}_w$,

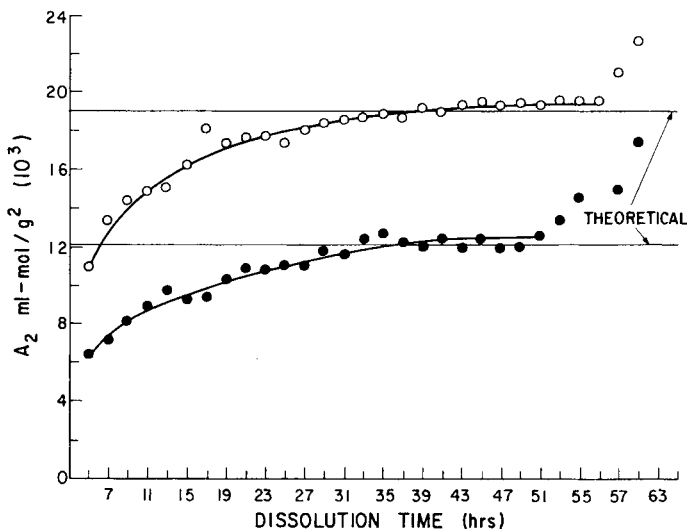Fig. 1.   Second virial coefficient (A_2, mL mol g^{-2}) vs. dissolution time at 145°C in TCB. The top curve is for a polypropylene with melt index 12 and $\overline{M}_w$ = 175,100, while the lower curve represents a polypropylene with melt index 3 and $\overline{M}_w$ = 235,800. The horizontal lines are the A_2 values calculated[5] from the cited $\overline{M}_w$ values and Mark–Houwink coefficients 1.50×10^{-2} mL/g and 0.76.

indicating the onset of significant chemical degradation. (Recall that these solutions contain added antioxidant as well as stabilizers that were present in the polymers as received.)

The foregoing results were confirmed and extended by GPC–LALLS measurements of $\overline{M}_w$ and $\overline{M}_z$ at 145°C in TCB following various storage times at that temperature in this solvent. Figure 2 shows the GPC values of $\overline{M}_z$ and $\overline{M}_w$ as a function of dissolution time for the higher molecular weight polypropylene. The corresponding plots for the lower molecular weight polymer are given in Figure 3.

In both cases there is a small increase in $\overline{M}_w$ during the first 10 h of solution time and a significant increase in $\overline{M}_z$ during the first 25–30 h. The observed increase in $\overline{M}_z$ is due to the progressive disaggregation of agglomerates. These clusters are not counted in the molecular weight analyses, either because they are filtered out in the GPC columns or, if they pass through the GPC, appear as "spikes"[4] in the LALLS trace. When the aggregates have been disrupted, the constituent large molecules are detected and $\overline{M}_z$ rises. The effect on $\overline{M}_w$ is less pronounced. An analogous effect has been noted with polyethylene aggregates.[4,6] $\overline{M}_z$ of the lower molecular weight samples reaches its equilibrium value after a shorter dissolution time than that of the lower melt flow index polypropylene.

After some 50–55 h at 145°C one can observe a drastic fall in $\overline{M}_z$, followed by a drop in $\overline{M}_w$. These changes, which indicate the onset of degradation, correspond to those noted on off-line light scattering measurements described above. It is clear that the procedure described provides a window of about 15–20 h, during which polypropylene solutions can be analyzed in stabilized TCB solutions at 145°C without interference from thermal degradation of the polymer.

The exact times needed for dissolution and freedom from degradation will vary somewhat with the polymer molecular weight distribution and the nature and concentration of stabilizers used in the analysis. Very high
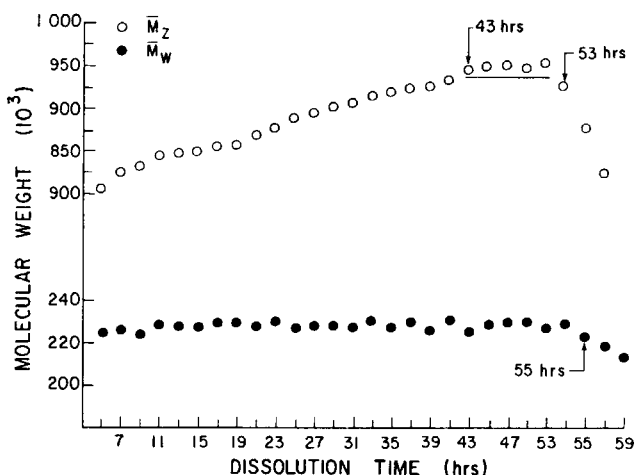

Fig. 2. $\overline{M}_z$ and $\overline{M}_w$ of melt flow index 3 polypropylene as a function of solution time in TCB at 145°C. Molecular weight averages are from GPC–LALLS measurements with solutions containing 0.1% (w/v) phosphite and 0.1% phenolic stabilizers.
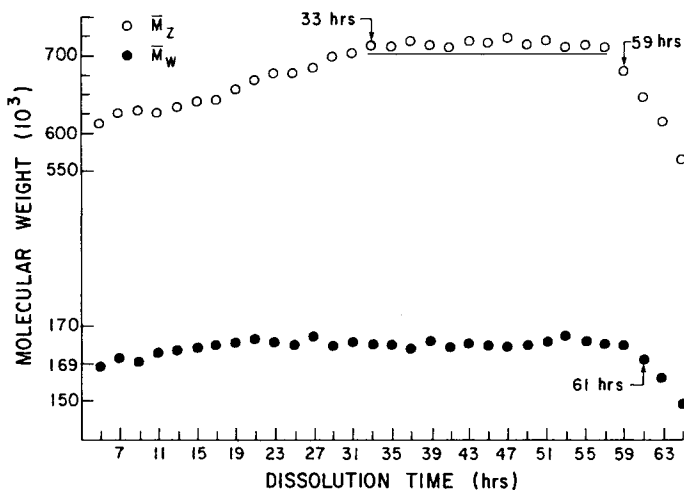
Fig. 3. $\overline{M}_z$ and $\overline{M}_w$ of melt flow index 12 polypropylene as a function of solution time in TCB at 145°C. Molecular weight averages are from GPC–LALLS measurements with solutions containing 0.1% (w/v) phosphite and 0.1% (w/v) phenolic stabilizers.

molecular weight polypropylenes may require a very careful procedure for measurement of reliable molecular weight averages.

CONCLUSIONS

1. Aggregates may exist in polypropylene solutions in TCB at 145°C. Measurements of $\overline{M}_z$ and higher averages of the molecular weight distribution are particularly compromised by the existence of such aggregates.

2. Dissolution procedures at temperatures higher than 145°C appear to be ineffective with polypropylene because of the limited thermal stability of this polymer.

3. Aggregate-free mixtures of polypropylene can be produced in TCB by controlling storage times at 145°C in stabilized solutions.

4. Light scattering experiments can be used to determine when aggregate-free solutions have been produced. This occurs when the measured second virial coefficient agrees with values predicted[5] for the $\overline{M}_w$ measured in the light scattering analysis.

5. Prolonged storage of polypropylene solutions at 145°C results in polymer degradation, which is evidenced by a sharp increase in the light scattering second virial coefficient.

6. GPC–LALLS measurements of $\overline{M}_w$ and $\overline{M}_z$ provide similar information about the effects of solution storage time on dissolution of aggregates and polymer degradation. $\overline{M}_z$ is a more sensitive indicator than $\overline{M}_w$, as measured by GPC–LALLS.

7. At 145°C, there appears to be a reasonably convenient time for molecular weight analyses between storage periods for deaggregation and the onset of significant amounts of polymer degradation. The duration of this analysis "window" appears to be inversely related to polymer molecular weight.

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